Grant AOARD 084131
Engineered Nanostructures for Optimal Strength and Toughness

Report for the period 9/8/08- 10/8/09
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Introduction

The original goal of this proposed work was to develop engineered nanostructures that could have extremely hard properties but yet adequate toughness approaching 20 MPa-m$^{1/2}$ to prevent fracture. In the first year of this work, understanding of both the necessary and limiting factors have been developed. Progress towards both high hardness and high toughness are reported along with appropriate metrics of publications and presentations.

Optimal Strength and Limitations

We now have an understanding of those parameters which control hardness and strength of nanoparticles and nanopillars made of nominally brittle oxides or semiconductors such as sapphire and silicon. These parameters are basically:

- size – smaller is stronger;
- dislocation nucleation – plasticity availability;
- confinement - plasticity is necessary but not sufficient;
- residual stress – states of stress could potentially represent a paradigm shift.

The overall effect is illustrated in Figure 1 for silicon single crystal nanospheres. A typical defect-free sphere made by the hypersonic plasma particle deposition technique is shown in Figure 1 (a). As evaluated by a combination of atomic force microscopy and

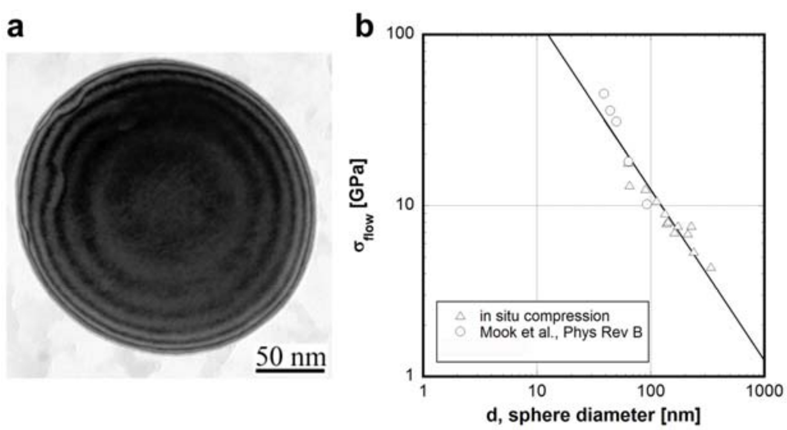

Fig. 1: A typical but larger than most spherical silicon crystal nanoparticles of this study is shown. (a) Electron microscopy image showing no defects but thickness fringe diffraction contrast; (b) Strength (mean contact pressure) as a function of sphere diameter.

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14. ABSTRACT
The goal of this proposed work was to develop engineered nanostructures that could have extremely hard properties but yet adequate toughness approaching 20 MPa-m1/2 to prevent fracture. In the first year (2008-2009) of this work, understanding of both the necessary and limiting factors have been developed. Progress towards both high hardness and high toughness are reported along with appropriate metrics of publications and presentations. Optimal Strength and Limitations: We now have an understanding of those parameters which control hardness and strength of nanoparticles and nanopillars made of nominally brittle oxides or semiconductors such as sapphire and silicon. These parameters are basically: ? size ? smaller is stronger ? dislocation nucleation ? plasticity availability ? confinement - plasticity is necessary but not sufficient ? residual stress ? states of stress could potentially represent a paradigm shift.

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in-situ transmission electron microscopy using either Triboindenters or PicoIndenters, the “smaller is stronger” feature has been found. . A decade increase in the contact stress (hardness) of these spheres is illustrated in Figure 1 (b). Current work is involved in demonstrating whether the plasticity is only due to dislocations or whether some pressure-induced phase transformation might also be involved. Indirectly, all current evidence points to dislocation nucleation. Regarding dislocation nucleation, a theoretical understanding leading to a modification of Christian’s nucleation model [1] is given by

$$\frac{V^*}{b^3} = \frac{\mu}{4k_T\tau}\left[\ln\left(\frac{\alpha V^*}{\pi b^3}\right)+1\right] \quad . \qquad (1)$$

Here μ/τ is the shear modulus to critical resolved shear stress for dislocation nucleation, k_T is a surface stress concentration factor, b is the Burgers vector and α is a dislocation core energy parameter. Given these, one can determine the normalized activation volume, V^*/b^3 for dislocation nucleation. For two reasons then, the size and surface condition must be appropriate for dislocation nucleation to achieve plasticity prior to brittle fracture in relative dislocation free small volumes. First, the size needs to be small enough to eliminate critical defect sizes for fracture. However, there must be nucleation sites, possibly with sufficiently high stress concentrations to nucleate dislocations but not fracture. Once dislocations nucleate, the flow stresses may increase further as long as the plasticity is constrained but not too immobilized. The confinement issue due to nanocrystalline grain sizes, dislocation substructures or oxide films as barriers to motion is still under investigation. Finally, a new consideration is the role of residual stresses where novel experiments of nanocrystalline SiC surrounding silicon nanopillars has demonstrated that substantial internal stresses can be developed. For example, we have demonstrated that Si/SiC, with a thermal expansion difference of $\Delta\alpha = 2\text{x}10^{-6}$/C can produce an extrusion of Si out of the core/shell nanocomposite during rapid thermal annealing (RTA). These four parameters should give considerable flexibility in optimizing possible strengths available.

Optimal Toughness and Limitations

Regarding fracture toughness, some progress has been achievable in monolithic materials, again single crystal silicon, but also coupled as a nanocomposite to SiC. For example, composite pillars of SiC/Si have been evaluated with cube-corner indenters to nucleate cracks. Such pillars shown in Figure 2 were then focused ion beam (FIB) cut to

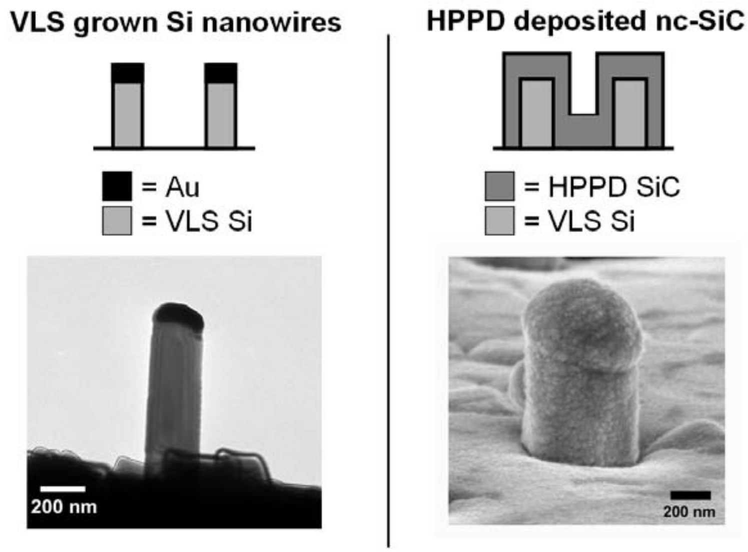

Figure 2: Silicon nanopillars coated with nanoparticle/CVD nanocomposites of SiC. These were initially grown by vapor-liquid-solid technique and coated by the HPPD process.

illustrate their cross-sections. As given in Figure 3(a), the indentation-induced cracks were utilized to measure the fracture toughnesses as indicated in Figure 3(b).

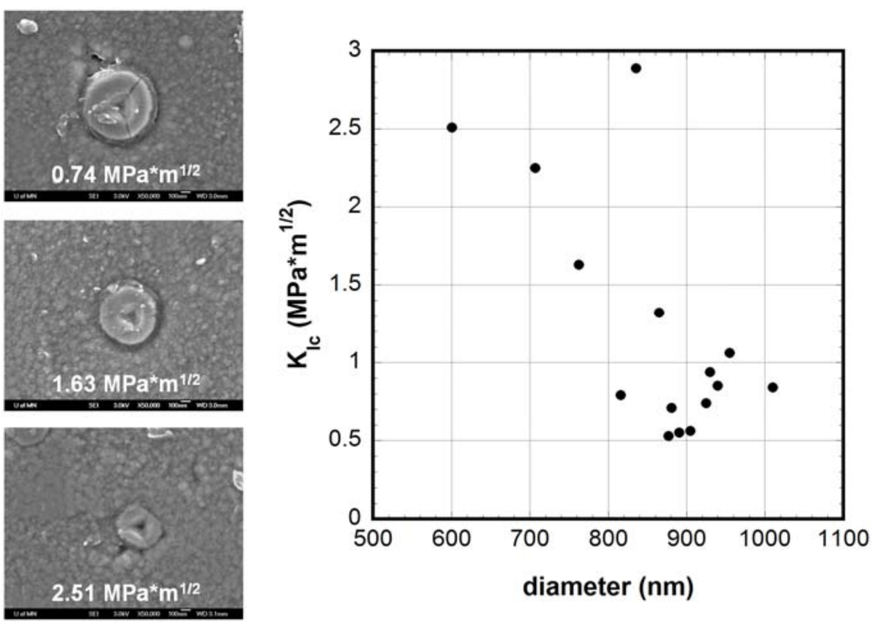

Figure 3: Different diameter nanocomposite nanopillars indented in Figure 3(a) give the results with others demonstrating the size effect of nanopillars on fracture toughness in Figure 3(b).

Here it is seen that the toughness increased brom bulk silicon (K_{Ic}= 0.7 MPa-m$^{1/2}$) for large diameter pillars, to about 2.5 MPa-m$^{1/2}$ for pillars about half the size of the larger

ones. As we had originally determined that the brittle-ductile transition at room temperature for silicon nanopillars was closer to 300 nm, subsequent evaluations will be produced for smaller nanopillars.

Program Metrics

Over the first year period of September 8 to October 8, 2009, the following publications and presentations associated with the grant resulted.

List of Refereed Publications:

1. F. Oestlund, K. Rzepiejewska-Malyska, K. Liefer, L.M. Hale, Y. Tang, R. Ballarini, W.W. Gerberich and J. Michler, "Brittle-to-ductile transition in uniaxial compression of silicon pillars at room temperature," Adv. Functional Materials, 19(2009) 2439-44.
2. L.M. Hale, X.W. Zhou, J.A. Zimmerman, N.R. Moody, R. Ballarini and W.W. Gerberich, "Molecular dynamics simulations of delamination of a stiff, body-centered-cubic crystalline film from a compliant Si substrate" J. Appl. Phys., 106 (2009) 083503/1-7.
3. N.Tymiak, D. Chrobak, W. Gerberich, O. Warren and R. Nowak, "Role of competition between slip and twinning in nanoscale deformation of Sapphire" Phys. Rev.B (2009) 174116/1-10.
4. M.J. Cordill, N.R. Moody and W.W. Gerberich, "The role of dislocation walls for nanoindentation to shallow depths," Intern. J. Plasticity, 25 (2009).

List of Invited Talks and Seminars:

1. "High nanoscale strength and toughness in ceramics," Departmental Seminar, University of Kentucky, May 13, 2009
2. "Nanoscale effects on brittle fracture" ICF 12, Ottowa Canada, July 15, 2009.
3. "Strength limitations: dislocations, transformation and the size effect," Berkeley Workshop, 8/11/09.
4. "Nanoscale flow and fracture: effect on the brittleness transition," Boston December 1, 2008.
5. "Size scale effects on dislocation nucleation and fracture," St. Thomas, Virgin I.,Jan.6, 2009.
6. A.R. Beaber, et al: "Residual stress toughening in ceramic nanocomposite coating deposited by hypersonic plasma particle deposition," Intern. Symp. On Plasma Chemistry, July 2009, Bochum, Germany.
7. A.R. Beaber, et al: Residual stress induced toughening in SiC nanocomposite coatings," Intern. Conf. on Adv. Ceramics and composites, Daytona Beach, Fl. Jan. 2009.